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Reactions of a *N*-Acyliminium Ion Pool with Benzylsilanes. Implication of a Radical/Cation/Radical Cation Chain Mechanism Involving Oxidative C−Si Bond Cleavage

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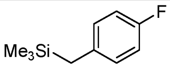
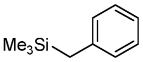
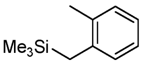
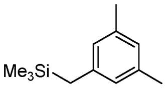
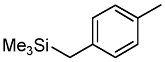
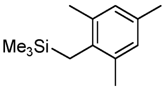
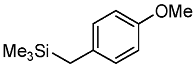
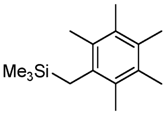
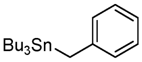
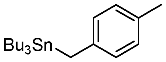
Mechanistic studies on the cleavage of the carbon−metal bond by the action of electrophiles have been carried out extensively so far, and the importance of a single electron transfer (SET) process[1] has been recognized not only for transition metal compounds but also for main group organometallics.[2] We have recently developed the "cation pool" method,[3] in which highly reactive organic cations are generated and accumulated in the absence of nucleophiles. Cation pools serve as powerful electrophiles toward various nucleophiles, including organosilicon and organotin compounds. Thus, we initiated our study to examine the possibility of a SET mechanism for the reaction of cation pools with such organometallic compounds.

We focused on the reactions of *N*-acyliminium ion pools[3a,c−e] because their reactions with various nucleophiles have been studied so far. Benzylsilanes were chosen to study as nucleophilic organometallics because benzylsilanes of various oxidation potentials can be easily synthesized by introducing electron-withdrawing or electron-donating groups on the benzene ring. Thus, several benzylsilanes were synthesized, and they were allowed to react with a pool of *N*-acyliminium ion **1**, which was generated by low-temperature electrochemical oxidation of the corresponding carbamate in Bu_4NBF_4/CH_2Cl_2 (Scheme 1).

Benzylsilanes **2a**−**c** did not react with *N*-acyliminium ion **1** as shown in Table 1 (runs 1, 4, and 5). Benzylsilanes of lower oxidation potentials, however, reacted with **1** to give the corresponding coupling products **3** (runs 6−7, 9−10, and 13), and 1.5 V seems to be the threshold point. Generally, benzylstannanes have lower oxidation potentials than the corresponding benzylsilanes. Thus, the reactions of benzylstannanes **8b** and **8e** with **1** were examined. As expected from the oxidation potentials, the reactions did take place to give **3** (runs 14 and 15).

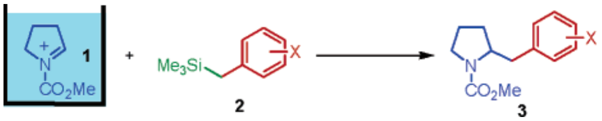
In order to test the possibility of a SET mechanism, the effect of a 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) free radical was examined for the reaction of **1** with **2g**. The reaction was inhibited completely in the presence 1 equiv of TEMPO (run 11). It is also noteworthy that 0.2 equiv of TEMPO was effective to inhibit the reaction completely (run 12). These observations imply that the reaction proceeds by a chain mechanism involving a free radical intermediate, although the possibility that TEMPO might retard other processes in the chain mechanism, such as a redox process, cannot be ruled out.

Table 1. Reactions of Benzylsilanes **2** and Benzenystannanes with a Pool of *N*-Acyliminium Ion **1**[a]

run	benzylsilane benzylstannane		oxidation potential (V)[b]	additive	product	%yield
1		**2a**	1.68	-		0
2				**8e** (0.1 equiv)[c]	**3a** **3e**	50 8
3				**8e** (1.0 equiv)[c]	**3a** **3e**	97 82
4		**2b**	1.68			0
5		**2c**	1.62			0
6		**2d**	1.59		**3d**	19
7		**2e**	1.55	-	**3e**	12
8				**8e** (0.1 equiv)	**3e**	97[d]
9		**2f**	1.48		**3f**	86
10		**2g**	1.37	-	**3g**	88
11				TEMPO (1.0 equiv)		0
12				TEMPO (0.2 equiv)		0
13		**2h**	1.36		**3h**	88
14		**8b**	1.24		**3b**	51
15		**8e**	1.16		**3e**	71

[a] Reactions were carried out with 0.2 mmol of benzylsilane **2** (or benzylstannane **8**) and 1.5 equiv of a pool of **1** at −50 °C for 1.5 h. [b] OSWV, in Bu_4NBF_4/CH_2Cl_2 using SCE as a reference electrode. [c] Slow addition. [d] The yield was based on **2e**. The yield based on the total amount of **2e** and **8e** was 88%.

Scheme 1



On the basis of the observations described above, we proposed a mechanism shown in Scheme 2. The initial SET from benzylsilane **2** to *N*-acyliminium ion **1** gives radical cation **4** and radical **5**.[4] The interaction of the C−Si σ orbital with the benzene π orbital increases the HOMO level to facilitate the electron transfer.[5] Because this process seems to be still energetically unfavorable, a possibility of photoinduced SET cannot be ruled out.[6] Another possibility to be considered is that the SET is promoted by the exoergonic follow-up reaction.[7] Radical cation **4** then collapses to benzyl radical **6** and a formal silyl cation. Such oxidative cleavage of C−Si bonds has been extensively studied in photochemical,[8] electrochemical,[9] and chemical[10] electron-transfer reactions. Because such cleavage is known to be promoted by nucleophilic attack on

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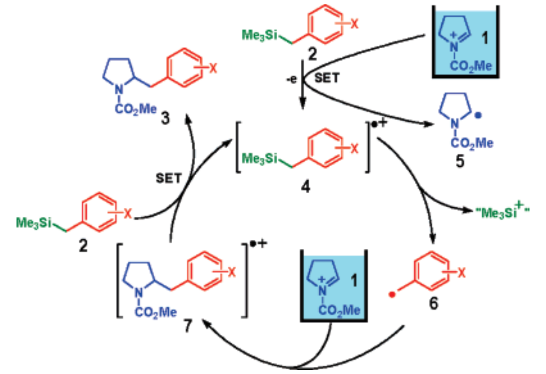
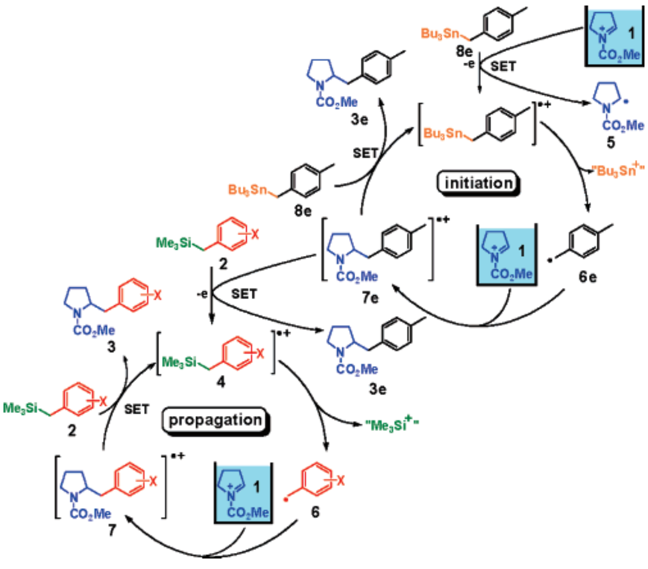
Scheme 2



Scheme 3



silicon,[11] the attack of BF_4^-, which is the counteranion of **1**, on silicon seems to play a significant role. Benzyl radical **6** thus generated adds to *N*-acyliminium ion **1** to give radical cation **7**.[12,13] We have already reported that an alkyl radical adds *N*-acyliminium ion pools very rapidly.[14] Radical cation **7** undergoes a SET reaction with benzylsilane **2** to give the coupling product **3** and radical cation **4**, which collapses to benzyl radical **6**. It is interesting that the present mechanism can be seen as the "umpolung" of the $S_{RN}1$ mechanism.[15]

As we have reported previously, DFT calculations indicated that the reduction of **7** to give **3** is thermodynamically more favorable than the reduction of **1** to radical **5**.[14] In other words, *the radical cation **7** is a stronger oxidant than the cation **1***. This idea prompted us to examine the following hypothesis: The use of a catalytic amount of benzylstannane **8**, which is more easily oxidized than benzylsilane **2**, as an initiator might lead to an effective chain reaction of benzylsilanes of high oxidation potentials. Radical cation **7**, which is generated by the reaction of **8** and **1**, might initiate the propagation cycle shown in Scheme 3. The hypothesis works. For example, the reaction of **2e** with **1** in the presence of 0.1 equiv of **8e** gave rise to the formation of coupling product **3e** in high yield (Table 1, run 8). Even *p*-fluorobenzylsilane **2a**, which has the highest oxidation potential among those examined, reacted with **1** in the presence of **8e** under the slow addition condition to give the desired coupling product **3a** together with **3e** (runs 2 and 3). It is important to note that the success of the present binary system also supports the proposed chain mechanism.

In conclusion, we have revealed that the reaction of a *N*-acyliminium ion pool with a benzylsilane proceeds by a chain mechanism involving oxidative C−Si bond cleavage. The success of the binary system consisting of a stoichiometric amount of a benzylsilane of high oxidation potential and a catalytic amount of a more easily oxidized benzylstannane opens a new possibility of promoting organometallic reactions that are otherwise difficult to achieve. Further work aiming at elucidation of the detailed mechanism and development of synthetic applications is in progress.

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Supporting Information Available: Experimental procedures and spectroscopic data of compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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